

Application No.: 10/678,766
Filing Date: October 2, 2003

REMARKS

Claims 1, 3-24, and 26-44 are pending in the present application. Applicant thanks the Examiner for the personal interview conducted on May 14, 2010. No claims are amended herein. Applicants respectfully request reconsiderations of the application in view of the above amendments and remarks below.

Applicants reattach the Declaration of Suvi Huakka and the Declaration of Marko Tuominen. The Declaration of Marko Tuominen was submitted in Serial No. 10/148,525, which includes an appendix with a description of the conditions used in the ALD experiments using SiCl₄ and other silicon containing precursors.

Rejection Under 35 U.S.C. § 103

Claims 1, 3-9, 11-24 and 26-41 have been rejected as obvious over “Surface Chemistry for Atomic Layer Growth” to George et al. (hereinafter “George”) in view of Sandhu et al. (U.S. Patent No. 6,313,035), Journal De Physique IV to Leskela et al. (hereinafter “Leskela”), U.S. Patent No. 6,015,590 to Suntola et al. (hereinafter “Suntola”) and “Aminosilane as a coupling agent...” to Juvaste et al. (hereinafter “Juvaste”). This rejection is respectfully traversed.

Applicant submits, as discussed during the interview, (1) that as stated in the Declarations by Suvi Haukka (see paragraph 9) and Marko Tuominen (see paragraph 8 and attached experimental results), the SiCl₄ used by George does not work to produce silicon oxide in a flow through reactor; (2) as a result a skilled artisan would not expect the combination of that process with a metal oxide process to produce a metal silicate in a flow-through reactor (Declaration of Suvi Haukka, paragraph 8). (3) The fact that it does work is surprising and supported by the specification and Declaration of Suvi Haukka (see paragraph 8); (4) The deposition rate of the claimed process was also surprising. For example, a particular silicon oxide process deposition rate was 0.2 Å/cycle and a metal oxide deposition rate was 0.2 Å/cycle. Thus, the expected growth rate for combining these processes would be 0.4 Å/cycle. However, the combination of those processes for a metal silicate produced a deposition rate of 0.7 Å/cycle (see Declaration of Suvi Haukka, paragraph 10).

Applicants believe that the rejections are based on a disbelief of the facts in the Declarations. Applicants submit that the Examiner is not free to ignore the facts stated in the

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Declarations. Further, the Examiner has not provided any evidence to counter the Declarations and therefore cannot base rejections on disbelief of the fact that SiCl₄ does not produce SiO₂ in a flow through reactor, nor the fact that the metal silicate deposition rate is higher than the sum of the individual silicon oxide and metal oxide deposition rates.

Applicants also point out that the Declaration of Marko Tuominen did include data detailing the experimental conditions used. Applicants have attached a copy of the Declaration including the experimental results.

George discloses a ‘static fill’ or ‘backfill’ reactor, which operates by contacting a substrate with a reactant and allowing the reactant to soak for *long exposure times*. (See Applicants’ Amendment and Declaration of Suvi Haukka filed April 20, 2009). Importantly, the reactant *is not flowing* during the exposure time. For example, George teaches exposure times of SiCl₄ and H₂O for as long as 72 minutes. (See George, page 13123). Applicants submit that George’s use of long static reactant exposure times to achieve deposition teaches away from using a reactor in which reactants *flow continuously*. Thus, George not only fails to teach or suggest a process in which reactants flow continuously from an inlet of the reactor to an outlet of the reactor, as in the pending claims, but actually teaches away from such a process.

Consistent with this, the SiCl₄ used by George does not work to produce silicon oxide in a flow through reactor when reactants flow continuously as recited in the claims. The Declaration of Marko Tuominen contains data for deposition runs using SiCl₄ and water. See paragraph 8 and the attached experimental results. The SiCl₄ pulses were 0.2 seconds followed by 0.8 second purges. The water pulses were 1.5 seconds followed by a purge of 2.0 seconds. The deposition temperature was 300°C and 100 deposition cycles were performed. No measurable film growth occurred after the substrate became covered with an initial SiO₂ surface. Declaration of Marko Tuominen, paragraph 8. Thus, Applicants submit that SiCl₄ and water does not appreciably grow SiO₂ when reactants are flowed continuously.

Thus, Applicants submit that the skilled artisan would not have expected the process of forming SiO₂ as disclosed in George et al. to even work in a flow type reactor, and that indeed, the inventors have experimentally found that SiO₂ does not grow appreciably in a flow type reactor. (See paragraphs 7-9 of the Declaration of Suvi Haukka). Applicants also refer to the low growth rates for other metal oxides in a flow type reactor observed by the inventors. (See

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paragraph 10 of the Declaration of Suvi Haukka). Thus, the skilled artisan would not have expected the SiO₂ process of George in combination with a metal oxide process to successfully produce a metal silicate in a flow-through reactor as recited in the claims. The unexpected results rebut any *prima facie* case of obviousness. (*See In re Soni*, 54 F.3d 746 (Fed. Cir. 1995))

Not only was any growth unexpected, but the high growth rate for metal oxides was even more unexpected. In view of the minimal or low growth rates for SiO₂ and metal oxides in a flow type reactor, the growth rates of metal silicon oxides were unexpectedly high, being considerably *higher* than the sum of the growth rates of each individual metal oxide and silicon oxide from which the metal silicon oxide is formed. (See paragraphs 10-15 of Declaration of Suvi Haukka). This result was surprising, because the skilled artisan would *not* have expected the growth rate of the claimed metal silicon oxide to be *any higher* than the sum of growth rates of each corresponding metal oxide and silicon oxide *combined*. Greater than expected results are evidence of non-obviousness. (M.P.E.P. 716.02(a) I; "Evidence of a greater than expected result may also be shown by demonstrating an effect which is greater than the sum of each of the effects taken separately (i.e., demonstrating "synergism"). *Merck & Co. v. Biocraft Laboratories*, 874 F.2d 804 (Fed. Cir), cert. denied, 493 U.S. 975 (1989)). The table in paragraph 11 of the Declaration of Suvi Huakka shows that the growth rate for each of the metal silicates is greater than the sum of the individual growth rate of the metal oxide plus the growth rate of SiO₂ using AMTMS (0.2 Å/cycle). (see Declaration of Suvi Haukka, paragraph 10). Applicants submit that only the inventors recognized the surprising results that SiO₂ not only grows surprisingly well on a metal oxide surface in a "flow type reactor" in the manner recited in the claims, but that the metal silicon oxide has an unexpectedly high growth rate. (see Declaration of Suvi Haukka, paragraphs 10-15).

As discussed above, the combination fails to disclose all of the features of the claims, there is no reason to make the combination, the references teach away from the combination, and the claims produced unexpected results. Accordingly, Applicants respectfully request withdrawal of the rejections to Claims 1, 22, 24 and 36.

Claims 3-9, 11-21, 23, 26-35 and 37-41 depend from Claims 1, 22, 24 and 36 and recite all the elements of Claims 1, 22, 24 and 36 in addition to reciting further distinguishing features.

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Thus, Applicants respectfully request withdrawal of the rejection of these claims as well, for at least the reasons set forth above.

Claim 10 is rejected as unpatentable over George in view of Sandhu, Leskela, Suntola and Juvaste, and further in view of U.S. Patent No. 5,891,744 to Lowrey et al. (hereinafter "Lowrey"). Claim 10 depends from Claim 1 and recites all the limitations of Claim 1 in addition to reciting further distinguishing features. Lowrey is only cited for allegedly disclosing deposition on a dielectric hemispherical grain area to form a capacitor. Lowrey doesn't provide any reason to disbelieve the results presented in the Declarations or to counter the teaching away in George. Thus, Applicants respectfully request withdrawal of the rejection to Claim 10 for at least the reasons set forth above.

Applicants submit that the Examiner cannot ignore facts provided in the Declarations without providing any reason or contrary evidence. Applicants submit that the facts in the Declarations support that the references teach away from the combination proposed by the Examiner. (It is improper to combine references where the references teach away from their combination. *In re Grasselli*, 713 F.2d 731, 743, 218 USPQ 769, 779 (Fed. Cir. 1983)). In addition, Applicants submit that the facts in the Declaration show unexpected results for the features recited in the claims. (M.P.E.P. 2141.01 V; *Graham v. John Deere Co.*, 383 U.S. at 17). Again, the Examiner has not provided any reason or contrary evidence to refute the evidence in the Declarations. Accordingly, as discussed above, the combination fails to disclose all of the features of the claims, there is no reason to make the combination, the references teach away from the combination, and the claims produced unexpected results. Accordingly, Applicants respectfully request withdrawal of the rejections.

No Disclaimers or Disavowals

Although the present communication may include alterations to the application or claims, or characterizations of claim scope or referenced art, Applicants are not conceding in this application that previously pending claims are not patentable over the cited references. Rather, any alterations or characterizations are being made to facilitate expeditious prosecution of this application. Applicants reserve the right to pursue at a later date any previously pending or other

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broader or narrower claims that capture any subject matter supported by the present disclosure, including subject matter found to be specifically disclaimed herein or by any prior prosecution. Accordingly, reviewers of this or any parent, child or related prosecution history shall not reasonably infer that Applicants have made any disclaimers or disavowals of any subject matter supported by the present application.

Please charge any additional fees, including any fees for additional extension of time, or credit overpayment to Deposit Account No. 11-1410.

Respectfully submitted,

KNOBBE, MARTENS, OLSON & BEAR, LLP

Dated: June 30, 2010

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant	:	Tois et al.
Appl. No.	:	10/678,766
Filed	:	October 2, 2003
For	:	METHOD OF GROWING OXIDE THIN FILMS
Examiner	:	Matthew J. Song
Group Art Unit	:	1722

DECLARATION OF SUVI HAUKKA UNDER 37 C.F.R. § 1.132

Dear Sir:

I, Suvi Haukka, do hereby declare and say as follows:

1. I am currently employed as an Executive Scientist for ALD applications for ASM Microchemistry Oy, in Helsinki, Finland. For the past nineteen years I have worked in various capacities including Research Scientist, Catalyst Technology Manager, Process Development Manager and R&D Manager which all have been related to atomic layer deposition (ALD). In particular, my work has focused on ALD and applications of it for semiconductor equipment, processes, and devices as well as development of ALD apparatus. Over the course of my career, I have been an author on over 60 scientific papers, primarily concerning ALD processes, applications and apparatus. In addition, I am an inventor of more than 60 patents and patent applications in the field of semiconductor fabrication. I am also listed as an inventor on the present patent Application. In 1994 I earned a Doctor of Philosophy degree from Laboratory of Analytical Chemistry, University of Helsinki, Finland.

2. I have read and understand the claims in the present patent application. I understand that the claims concern processes for producing a thin metal silicon oxide ($MSiO_x$) film on a substrate comprising contacting a substrate with a vapor phase silicon compound, contacting the substrate with a vapor phase metal compound, and converting adsorbed

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compounds on the substrate into MSiO_x by contacting them with a reactive vapor phase oxygen source, in the manner recited in independent Claims 1, 22 and 36, and adsorbing a layer of a silicon compound on a substrate in a flow type reactor, adsorbing a layer of a metal compound on a substrate, and converting the adsorbed compounds into a tertiary metal silicon oxide by contact with a reactive vapor phase oxygen source compound, in the manner recited in independent Claim 24.

3. I am familiar with the course of prosecution of the present patent application, including the Office Action mailed on November 18, 2008, in which George et al. ("Surface Chemistry for Atomic Layer Growth"), Sandhu et al. (U.S. Patent No. 6,313,035), Leskela et al. (Journal De Physique IV) and Suntola et al. (U.S. Patent Nos. 6,015,590) were discussed. I understand that the Examiner concluded that the skilled artisan would understand George et al. read in conjunction with Sandhu et al., Leskela et al. and Suntola et al. to render obvious ALD processes for producing metal silicon oxide films as claimed. For the reasons detailed below, I disagree with this conclusion.

4. As an expert in the field of semiconductor fabrication, I had an understanding of the scientific and engineering principles applicable to equipment for thin film deposition, particularly for CVD and ALD, at the time the present application was filed.

5. Independent Claims 1, 22, 24 and 36 have been currently amended to recite a 'flow type reactor.' It is my opinion that at the time of the invention, the ordinary engineer would have understood a 'flow type reactor' as a reactor in which reactants and/or inert gases are separately flowed through the reactor during the ALD deposition cycle where the reactor is continuously pumped. This is in contrast to a reactor that has its outlet closed during reactant pulses in order to 'soak' the substrate in the reactant for prolonged periods.

6. George et al. does not teach a 'flow type' reactor but a 'backfill' reactor, which operates by closing the exhaust and allowing reactants to fill the reactor and contact a substrate over the course of long exposure times. Consistent with this, George et al. teaches that substrates were exposed to SiCl_4 and H_2O for SiO_2 growth for as long as 72 minutes, and to TMA and H_2O for Al_2O_3 growth for as long as 200 seconds. (Figures 2-4 and 7-8, page 13123-13124).

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7. I would not have expected the process for depositing SiO₂ disclosed in George et al. to work in a flow type reactor. Instead, I would have understood that the reaction between SiCl₄ and H₂O is kinetically slow, and that long reaction times in a closed system would be necessary to achieve growth of SiO₂ films. Again, consistent with this, George et al. teaches that long exposure times of several minutes were used to achieve SiO₂ growth from SiCl₄ and H₂O. (Figure 2-4, page 13123). The teachings of George et al. would have indicated to a skilled artisan at the time of our invention that full surface reactions require the long and undisturbed reactant exposure provided by ‘backfill’ reactors.

8. It is also my opinion that the skilled artisan would not have expected commercially viable growth of a metal silicon oxide film in a flow type reactor, based on the lack of appreciable SiO₂ growth in a flow type reactor, and the growth rates that were experimentally observed in a flow type reactor for individual metal oxides, as described below.

9. For example, we found that slow or no SiO₂ film growth occurs by ALD in a flow type reactor using conventional silicon precursors. In particular, we found that using SiCl₄ and H₂O does not produce appreciable SiO₂ film growth by ALD in a flow type reactor. These results have been submitted by my co-inventor Marko Tuominen in a Declaration to the United States Patent and Trademark Office dated November 29, 2007, for related Application No. 10/148525. (See paragraph 8 of the attached Tuominen Declaration and attached experimental results).

10. The low growth rates of single metal oxides have also been highlighted to the Examiner in a table, reproduced below, comparing the growth rates of metal silicon oxides and their respective metal oxides, in Applicants’ Response to Final Office Action, mailed October 31, 2007. As noted on page 8 of the Response, the following growth rates were reported in the literature for single metal oxides (other than SiO₂) deposited by ALD using the listed metal precursors. I confirm that we observed the growth rates for the metal silicon oxides and the silicon oxide listed in the table by ALD using the same metal precursors in a flow type reactor.

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The differences between the sum of the listed growth rates for the metal oxide and silicon oxide, and the growth rate for the corresponding metal silicon oxide, were not expected:

Oxide	Growth Rate Å/c	Metal Silicon Oxide	Growth Rate Å/c
TiO ₂ from TiCl ₄	0.5	SiTiO _x	0.9
Ta ₂ O ₅ from TaCl ₅	0.43	SiTaO _x	1.1
HfO ₂ from HfCl ₄	0.5	SiHfO _x	1.23
ZrO ₂ from ZrCl ₄	0.5	SiZrO _x	1.1
La ₂ O ₃ from La(thd) ₃	0.36	SiLaO _x	0.75
Y2O ₃ from Y(thd) ₃	0.23	SiYO _x	0.73
SiO ₂ from AMTMS	0.2		

11. George et al. also teaches HfO₂ deposition from HfCl₄ + H₂O and SiO₂ deposition from SiCl₄ + H₂O. (Page 13122). As discussed above, we have found experimentally that while George et al. was able to achieve SiO₂ growth in their closed system, there is no appreciable growth of SiO₂ from SiCl₄ and H₂O in a flow type reactor. We have also found HfO₂ can be grown in a flow type reactor from HfCl₄ and H₂O with a growth rate of about 0.5 Å/cycle. Even if the teachings of George et al. about single oxide depositions using long exposure times in a 'backfill' reactor were relied on, prior to the present invention I would not have expected it to be possible to incorporate SiO₂ in HfO₂ to form hafnium silicate by using HfCl₄ + H₂O and SiCl₄ + H₂O processes in a flow type reactor, because SiO₂ does not grow appreciably in a flow type reactor.

12. Surprisingly, and contrary to what was expected, we have found that hafnium silicate grows very well by using HfCl₄ + H₂O and SiCl₄ + H₂O in a flow type reactor. Hafnium silicate films made by using a 1:1 (HfO₂):(SiO₂) cycle ratio from HfCl₄ + H₂O and SiCl₄ + H₂O comprised about 9-13 at-% of silicon, about 15-19 at-% of hafnium and 69-72 at-% of oxygen, as measured by Electron Spectroscopy for Chemical Analysis (ESCA), which is also known as X-ray photoelectron spectroscopy (XPS), after sputtering the contaminants from air. The results of this analysis are submitted with this Declaration. Moreover, the specification of related Application No. 11/868,333 also provides further evidence that hafnium silicate can be grown using HfCl₄, SiCl₄ and H₂O as precursors in a flow type reactor (Pulsar® reactor manufactured by ASM America, Inc.). (See Application No. 11/868,333, pages 12-15).

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13. Thus we have found that while SiO_2 grows slowly or not at all on SiO_2 surfaces in a flow type reactor, it grows very well when there is a metal oxide surface on the substrate, which affects the silicon precursor reaction on the growing surface. Again, achieving growth of a metal silicon oxide film in a flow type reactor was unexpected because the skilled artisan would not have expected any appreciable silicon oxide, a component of the metal silicon oxide, to grow on the substrate in a flow type reactor.

14. Prior to the invention, the ordinary engineer would have expected the growth rate of a metal silicon oxide to be equal to the growth rate of its corresponding metal oxide and the growth rate of silicon oxide. However, not only did we surprisingly find that metal silicon oxides can be grown in a flow type reactor, we have also unexpectedly found that the growth rate for metal silicon oxides in a flow type reactor is much higher than the sum of the growth rate of metal oxide and the growth rate of silicon oxide, which would have been the expected growth rate for the metal silicon oxide.

15. We have unexpectedly found that the growth rate for metal silicon oxides in a flow type reactor is even higher than what one would have expected by combining the growth rates of the individual oxides from which the metal silicon oxide is formed. For example, we have found a growth rate of about 0.5 \AA/cycle for HfO_2 (using HfCl_4) and in the range of about 0.16 to about 0.2 \AA/cycle for SiO_2 (using 3-aminopropyltrimethoxy silane). Thus, a growth rate in the range of about 0.66 to 0.70 \AA/cycle would have been expected for HfSiO_x (using a combination of HfO_2 and SiO_2 reactions). However, a growth rate of 1.23 \AA/cycle was achieved instead, which is more than a 75% unexpected increase. (See Example 2 of Application). Thus, the growth rate of the metal silicon oxide was even higher than expected from combining the growth rates of the individual oxides from which the metal silicon oxide is formed.

16. In essence, we have observed that a 'boost' in growth rate for metal silicates occurs when there is a metal oxide surface present, which affects the silicon precursor reaction on the growing surface. This 'boost' does not occur in the growth of individual oxides. The increase in silicon precursor reactions in the presence of a metal oxide surface is surprising and was not expected.

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17. Example 2 of the Application also reports unexpectedly high growth rates for metal silicon oxides of six different metals. Based on these results, I would conclude that the increase in growth rate for metal silicon oxides over that of each individual oxide from which the metal silicon oxide is formed is a phenomenon that occurs generally for all metal silicon oxides over their respective individual oxides.

18. The Examiner incorrectly believes that complete reactions would be expected produce the maximum growth rate of approximately 1.1 Å/cycle and that Applicants' growth rate of 0.2 Å/cycle represents "incomplete half-reactions." (Final Office Action, page 10). I disagree with the Examiner's allegation. Atomic layer deposition (ALD), or atomic layer epitaxy (ALE) as it is referred to by George, is based on saturated and complete surface reactions of chemicals (that do not decompose on the surface) with reactive surface sites. However, all ALD processes will produce unique growth rates, depending on the particular chemicals used, deposition temperatures and many other factors. The different factors that determine the overall growth rate include, among other things, the size of the precursor molecules, the density of the reactive surface sites (*e.g.*, OH-groups) that determines where the precursor can react on the surface, and all the various stereochemical configurations and molecular arrangements that can occur on the depositing surface. Thus, SiO₂ deposition processes using different silicon precursors or deposition parameters can have very different growth rates. The SiO₂ growth rate we found of about 0.2 Å/cycle does represent that of complete, saturating reactions, and not "incomplete half reactions," as the Examiner has incorrectly alleged. Thus, it is appropriate to compare the growth rates achieved for metal silicon oxides to that of the growth rates of individual oxides in arriving at the conclusion that the growth rate of the metal silicon oxide is surprisingly higher than that expected from the individual oxides.

19. Prior to the present patent application of Tois et al., I was not aware of any process for producing a metal silicon oxide film by contacting a substrate in a flow type reactor with a vapor phase silicon compound, a vapor phase metal compound and a reactive vapor phase oxygen source in the manner claimed in Claims 1, 22 and 36, and adsorbing a layer of a silicon compound on a substrate in a flow type reactor, adsorbing a layer of a metal compound on the substrate, and converting the adsorbed compounds into a tertiary metal silicon oxide by contact with a reactive vapor phase oxygen source compound, in the manner claimed in Claim 24.

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20. For the reasons noted above, I would not have modified the disclosures in George et al., Leskela et al. and Suntola et al. to produce metal silicon oxide films on a substrate in a flow type reactor in the manner claimed, much less expect the increase in growth rate observed.

21. Further, I would not have expected the commercially viable results we obtained in producing metal silicon oxide films on a substrate in a flow type reactor in the manner claimed.

22. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true. I declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,

Dated: March 31, 2009

By: S. Haukka

Suvi Haukka

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Tois et al.
Appl. No. : 10/148,525
Filed : August 27, 2002
For : METHOD OF GROWING OXIDE FILMS
Examiner : Matthew J. Song
Group Art Unit : 1722

DECLARATION OF MARKO TUOMINEN UNDER 37 C.F.R. § 1.132

Dear Sir:

I, D.Sc. (Tech.) Marko Tuominen, do hereby declare and say as follows:

1. I have worked in various capacities from process engineer and project manager to R&D manager in the area of semiconductor equipment, processes, and devices. In particular, my work has focused on atomic layer deposition processes, apparatus and device integration of integrated circuits. I am currently a General Manager of ASM Microchemistry Oy in Helsinki, Finland where I manage an R&D organization focused on atomic layer deposition processes, equipment and applications of those processes primarily for the semiconductor industry. Over the course of my career, I have been an author on more than 50 papers concerning both atomic layer deposition and silicon carbide deposition. In addition, I am an inventor on various patents in the field of semiconductor fabrication. I am also listed as an inventor on the present patent Application. Prior to my work in the field of atomic layer deposition, I earned a Doctor of Science (Technology) degree, which is equivalent to a Ph.D., from Linköping University, Linköping, Sweden.

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2. I have read and understand the claims in the present patent application. I understand that the claims concern atomic layer deposition (ALD) processes for producing a thin film comprising silicon dioxide (SiO_2) on a substrate by alternating, saturating surface reactions, which comprises contacting a substrate with a vaporized silicon compound selected from the group consisting of amino substituted silanes and silazanes.

3. I am familiar with the course of prosecution of the present patent application, including the Office Action mailed on June 1, 2007, in which U.S. Patent No. 6,090,442 (referred to as "Klaus et al."), JP 06-0804413 (referred to as "Maruyama") and JP 03-082769 (referred to as "Tanaka") were discussed. I understand that the Examiner concluded that the ordinary engineer would understand Klaus et al. read in conjunction with Maruyama or Tanaka to render obvious ALD processes for producing SiO_2 films by contacting a substrate with a vaporized silicon compound selected from the group consisting of amino substituted silanes and silazanes. For the reasons detailed below, I disagree with this conclusion.

4. As an expert in the field of semiconductor fabrication, and particularly atomic layer deposition (ALD), prior to the present patent application of Tois et al., I was not aware of any ALD process for producing a SiO_2 film by contacting a substrate with amino substituted silanes and silazanes.

5. Prior to research conducted by the inventors in the present application, it is my opinion that the ordinary engineer would not have considered the use of amino substituted silanes and silazanes in ALD methods for producing SiO_2 films. The references cited in the present application do not provide any indication that amino substituted silanes and silazanes can be used for forming SiO_2 films by ALD.

6. I have read and understood Klaus et al. I understand that Klaus et al. discloses methods of forming atomic layer thin films. Moreover, I understand that Klaus et al. teaches that growth of SiO_2 films is not observable when using a SiCl_4 precursor with water in a closed reaction chamber, unless a catalyst (pyridine) is added to activate the surface species and lower the required reaction temperature, as described in Col. 7, lines 34-39 and 50-54. I also

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understand that there is no teaching in Klaus et al. that SiO₂ film growth by ALD methods would even be possible without the use of a catalyst to initiate or enhance film growth. Moreover, Klaus et al. teaches that even if a catalyst is used to enhance film growth, SiO₂ film growth is still very slow, with reaction cycles requiring times longer than 75 seconds for completion, as described in Col. 7 line 34 to Col. 8 line 4. It is my opinion that even with the use of a catalyst to enhance film growth, it would not be commercially feasible to use the methods of Klaus et al. to form SiO₂ films on an industrial scale based on the reaction time disclosed.

7. It is also my opinion that the ordinary engineer would not have expected conventional CVD silicon precursors to automatically work in ALD reactions and in particular would not have expected conventional CVD silicon precursors to work for forming SiO₂ films by the ALD process disclosed in Klaus et al., much less to produce a commercially acceptable rate of reaction. Indeed, the inventors have found that the growth of silicon dioxide by ALD using various conventional silicon CVD precursors, including SiCl₄, tetramethylorthosilicate ("TMOS") or tetraethylorthosilicate ("TEOS"), is very slow or does not occur at all under the ALD conditions tested.

8. Indeed, the inventors specifically experimented with numerous conventional CVD precursors and found that many of them do not work in particular ALD processes. For example, experiments were conducted using the same precursors with which Klaus et al. experimented, and confirmed that when SiCl₄ and water were used without any catalyst in a 'flow-type' ALD reactor, no measurable SiO₂ film growth occurred after the substrate became covered with an initial SiO₂ surface. These experimental results, indicating a "run date" of February 17, 2003, are included with this Declaration. Similarly, experiments using the conventional CVD precursors tetramethylorthosilicate ("TMOS") or tetraethylorthosilicate ("TEOS") in ALD processes showed no measurable film growth. Experimental results using TMOS and water with run dates of June and July of 2000 are also included with this Declaration. Experiments using the CVD precursor tetrakisdimethylaminosilane ("TDMAS") with water also resulted in no film growth (although it did work with ozone). Further, experimental results using TDMAS and water or ozone with run dates of August of 2000 are also included with this Declaration. These results support the conclusion that CVD precursors would not be expected to automatically work

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in ALD processes and in particular would not be expected to be useful in growing SiO₂ films by ALD.

9. I have read and understood the translation of Maruyama and the translation of the abstract of Tanaka. I understand that Maruyama discloses a method of forming SiO₂ films by CVD with the silicon precursor tetrakisdimethylaminosilane and that Tanaka discloses a method of forming SiO₂ films by UV irradiation with the silicon precursor hexaalkyldisilazane. I understand that Maruyama and Tanaka do not use and in no way suggests the use of amino substituted silanes and silazanes in ALD methods for forming SiO₂ films. I further understand that there is no teaching or suggestion in Klaus et al., Maruyama or Tanaka, that the tetrakisdimethylaminosilane disclosed in Maruyama or the hexaalkyldisilazane disclosed in Tanaka could be used in ALD methods for forming SiO₂ films.

10. The inventors have discovered that SiO₂ films can unexpectedly be grown on a substrate at industrially acceptable rates without the addition of a separate catalyst to initiate or enhance growth. This result was surprising and would not have been anticipated by the ordinary engineer.

11. In my opinion, after reading Klaus et al. and the various CVD references of record, the skilled artisan would have had no reason to expect that amino substituted silanes and silazanes could be successfully used as silicon precursors in the ALD processes of Klaus et al., or that they would improve upon the results obtained by Klaus et al. to allow deposition of SiO₂ films by ALD at a commercially viable rate.

12. For the reasons noted above, it is my considered opinion that the ordinary engineer would not have combined the disclosures in Klaus et al. and Maruyama or Tanaka, or made any other combination of the cited references to use amino substituted silanes and silazanes to form SiO₂ films and, further, would not have expected the commercially viable results obtained by the inventors.

Appl. No. : 10/148,525
Filed : August 27, 2002

13. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true. I declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,

Dated: Nov. 29, 2007

By: Marko Tuominen

Marko Tuominen

4584845
112807

Attachment to Declaration of Marko Tuominen

Date	Oper.	Run X #	Film	Temp. °C	Wafer 100 mm Si	M-Pre	O-Pre	[1 s]	O-Fre	[1 s]	Thicknesses [Å]	Comments
					n-type wafer out of box	Pulse 1	Purge 1	Pulse 2	Purge 2	Cycles	Aver. Cente Max Min A/Cycle	
24-Aug-00	EAR,TMA	2159	SiO2	350	n-type wafer out of box	TDMAS	H ₂ O	1.0	1.5	1.0	1000	No film
30-Aug-00	JMA	2164	SiO2	350	n-type wafer out of box	TDMAS	O ₃	1.0	1.5	2.0	4.0	tetrakisdimethylaminosilane

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Date	Run	Material	Deposition Temp. (°C)	Pulse Length for precursor 1 (s)	Pulse Length for precursor 2 (s)	Source/Temp. (°C)	Number of Cycles	Mean Growth Rate (Å/Cycle)	Precursor consump. (g)	FilmMax / nm	FilmMin / nm	FilmMean / nm	FilmRange / nm
2/14/2003	N-1783	SiO ₂	300	SiCl ₄	0.2/0.8	H ₂ O 1.5/2.0	SiCl ₄ RT	100	0	3.1	9	0.00	0.00
2/14/2003	N-1784	SiO ₂	300	SiCl ₄	0.2/0.8	H ₂ O 1.5/2.0	SiCl ₄ RT	100	0	1	9	0.00	0.00
2/17/2003	N-1785	SiO ₂	300	SiCl ₄	0.2/0.8	H ₂ O 1.5/2.0	SiCl ₄ RT	100	0	0.6	g	0.00	0.00
2/17/2003	N-1786	SiO ₂	300	SiCl ₄	0.2/0.8	H ₂ O 1.5/2.0	SiCl ₄ RT	100	0	0.5	g	0.00	0.00

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Pvm	Operator	run X #	film	Temp. [°C]	substrate 100 nm Si	M-Precursor	T. source [°C]	consumption	O-Precursor	M-Pre Pulse 1	[1 s] purge.1	O-Pre Pulse 2
20-Jun-00	JMA	2136	SiO2	400	n-type wafer out of box	Si(OMe)	30	1.00	H ₂ O	0.5	1.0	2.0
21-Jun-00	JMA	2137	SiO2	400	n-type wafer out of box	Si(OMe)	30	1.00	H ₂ O	0.5	1.0	2.0
22-Jun-00	JMA, TAA	2138	SiO2	400	n-type wafer out of box	Si(OMe)	30	1.00	H ₂ O	0.5	1.0	2.0
26-Jun-00	EAR, TAA	2139	SiO2	400	n-type wafer out of box	Si(OMe)	RT	4.1 g	H ₂ O	2.0	1.0	2.0
27-Jun-00	EAR, TAA	2140	SiO2	400	n-type wafer out of box	Si(OMe)	RT	0.7 g	H ₂ O	2.0	1.0	10.0
28-Jun-00	EAR, TAA	2141	SiO2	300	n-type wafer out of box	Si(OMe)	RT	2.8 g	H ₂ O	3.0	1.0	10.0
29-Jun-00	EAR, TAA	2143	SiO2	300	Al2O ₃ 53 Å on Si	Si(OMe)	RT	1.8 g	H ₂ O	2.0	1.0	10.0
30-Jun-00	EAR, TAA	2144	SiO2	300	n-type wafer out of box	Si(OMe)	RT	1.5 g	H ₂ O	3.0	1.0	2.0
3-Jul-00	EAR, TAA	2146	SiO2	400	Al2O ₃ on Si	Si(OMe)	RT	5.1 g	H ₂ O	3.0	1.0	10.0
4-Jul-00	EAR, TAA	2148	SiO2	400	Al ₂ O ₃ 14 nm on Si	Si(OMe)	RT	5.9 g	H ₂ O	2.0	1.0	10.0
5-Jul-00	EAR, TAA	2149	SiO2	400	n-type wafer out of box	Si(OMe)	RT	0.1 g	H ₂ O	2.0	1.0	10.0

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[1 s] purge,2	cycles	thicknesses [Å]	Center	Max	Min	Uf [%]
2.0	1140					
2.0	2000					
2.0	1698					
2.0	2000					
2.0	265					
2.0	1000					
2.0	1000					
1.0	1000					
1.0	1000					
2.0	1000					
2.0	2000					
2.0	1500					